UNVEILING THE CONSEQUENCES OF COMPLETE SUBSTITUTION OF Sn ATOMS FOR Ni ATOMS IN $LaNi_5$: A DFT PERSPECTIVE

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Abstract

The intermetallic compound $LaNi_5$ is a promising material for hydrogen storage. The ternary phase diagram La-Ni-Sn contains phases in which Ni atoms are substituted by Sn atoms, resulting in several different Sn/Ni ratios. In order to describe the $La(Ni,Sn)_5$ system by phenomenological CALPHAD modelling, the energy of the completely substituted $LaSn_5$ is needed. As this compound does not exist under ambient conditions, it is difficult to examine experimentally. Therefore, its properties were computed by quantum-mechanical calculations. Density functional theory (DFT) was employed to determine the structural characteristics of $LaSn_5$, along with its electronic structure, energetics and thermodynamic stability as well as its mechanical stability. Our DFT calculations revealed a dramatic volume expansion upon this extreme case of substitution of all Ni atoms by Sn atoms, but the hexagonal structure remains stable without any significant distortions. The electronic calculations also revealed that the electronic density of states has a minimum at the Fermi level, which is in line with the lattice stability.

Keywords: La-Ni-Sn, quantum-mechanical calculations, stability, thermodynamics, elasticity

1. INTRODUCTION

Effective energy storage remains a critical obstacle in the full-scale transition to renewable energy sources, with hydrogen storage standing out as a particularly promising technology. Metal hydrides represent a viable class of materials for this application, offering high volumetric hydrogen density and advantageous safety features. Binary La-Ni intermetallic compounds, often derived from the $LaNi_5$ compound, exhibit noteworthy structural and electronic characteristics particularly relevant for hydrogen storage and other energy-related technologies [1, 2]. The properties of these materials can be systematically tailored through alloying and the substitution of individual atomic species [3]. Such modifications can significantly alter the crystal structure and lattice parameters, thereby playing a crucial role in determining hydrogen absorption behaviour [4]. However, there is a limited understanding of the stability and existence of complex intermetallic phases within the broader La-Ni-Sn systems. This lack of data, particularly concerning terminal compounds, negatively affects the development of advanced storage-related hydrides and the accuracy of thermodynamic modelling approaches like CALPHAD.

The present study addresses this data gap by focusing on the complete substitution of the Ni sub-lattice with Tin (Sn), exploring the hypothetical $LaSn_5$ compound. We employ a quantum-mechanical approach based on Density Functional Theory (DFT) to explore the equilibrium characteristics, electronic structure, and the thermodynamic and mechanical (elastic) stability of the hexagonal $LaSn_5$ phase. The results provide critical reference data necessary for robust modelling of phase equilibria in the La-Ni-Sn system.

2. COMPUTATIONAL METHODOLOGY

Our first-principles calculations were performed using the Vienna Ab initio Simulation package (VASP) [5,6] within the Density Functional Theory (DFT) [7,8] employing Projector Augmented Wave (PAW) [9,10] pseudopotentials (an 11-valence-electron La potential and a 14-valence-electron Sn potential from the potpaw_PBE.64 VASP database). The exchange-correlation energy was approximated by the Generalized Gradient Approximation (GGA) as parametrized by Perdew, Burke and Ernzerhof (PBE'96) [11]. To ensure high accuracy, the plane-wave energy cut-off was set to 870 eV. We used the Methfessel-Paxton smearing scheme (ISMEAR) of order 1 with the smearing parameter (SIGMA) set to 0.095. The reciprocal space was sampled using k-point mesh generated by VASP INCAR file KSPACING = 0.1. The structural model of the hypothetical $LaSn_5$ compound was obtained by substituting all Ni atoms in the hexagonal *P*6/*mmm* $LaNi_5$ structure with Sn atoms. Single-crystal elastic constants were computed by the stress-strain method [12].

3. RESULTS

Our calculations started with a full structural relaxation, optimizing all degreed of freedom for the cell, i.e., atomic positions, cell shape and volume. The resulting minimum-energy structure retains the hexagonal $CaCu_5$ prototype *P*6/*mmm* (**Figure 1**). The optimized lattice parameters are equal to $a = b = 6.243$ Å and $c = 5.425$ Å and the unit cell volume is 183.11 Å^3. Comparing this result to the experimentally verified reference volume of $LaNi_5$ ($V = 86.91$ Å^3) [13], the complete substitution of the smaller Ni atoms with the larger Sn atoms leads to a substantial lattice volume expansion by over 110 %. This massive expansion is the fundamental consequence of the complete substitution.

The thermodynamic stability of hypothetical compound $LaSn_5$ was assessed by evaluating their formation energy ΔE_f. Its mathematical expression is specifically for $LaSn_5$ as follows:

$$\Delta E_f(\mathrm{LaSn_5}) = \frac{E(\mathrm{LaSn_5}) - E(\mathrm{La}) - 5 \cdot E(\mathrm{Sn})}{1+5},$$

where we used the static-lattice energy $E(\mathrm{LaSn_5})$ of the $LaSn_5$ and energies of constituting pure elements in their ground-state structures, in particular, $E(\mathrm{La})$ for the non-magnetic hexagonal close-packed (hcp) La and $E(\mathrm{Sn})$ for the non-magnetic *α*-Sn phase with the diamond crystal structure.

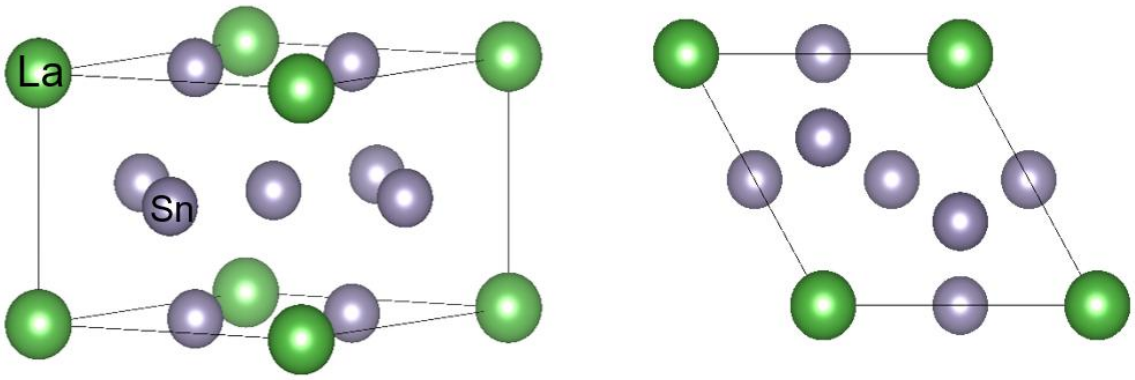

Figure 1 Visualizations of the hexagonal cell of $LaSn_5$.

The computed formation energy is equal to -0.107 eV/atom (-10.3 kJ/mol atom). This value serves as the essential thermodynamic input required for the further CALPHAD modelling of the La-Ni-Sn system.

To gain insight into the bonding character and the local stability mechanisms, the Electron Localization Function (ELFCAR) was analysed, see **Figure 2**. There are no areas with high ELF values (i.e., ELF>0.8) localized between the La and Sn atoms, ruling out strong covalent or ionic interactions as the primary stabilizing factor. The majority of the bonding regions exhibit ELF values close to 0.5 (represented by the green areas in **Figure 2**), confirming the presence of a delocalized electron sea characteristic of metallic systems. It is also the primary mechanism stabilising the highly expanded compound.

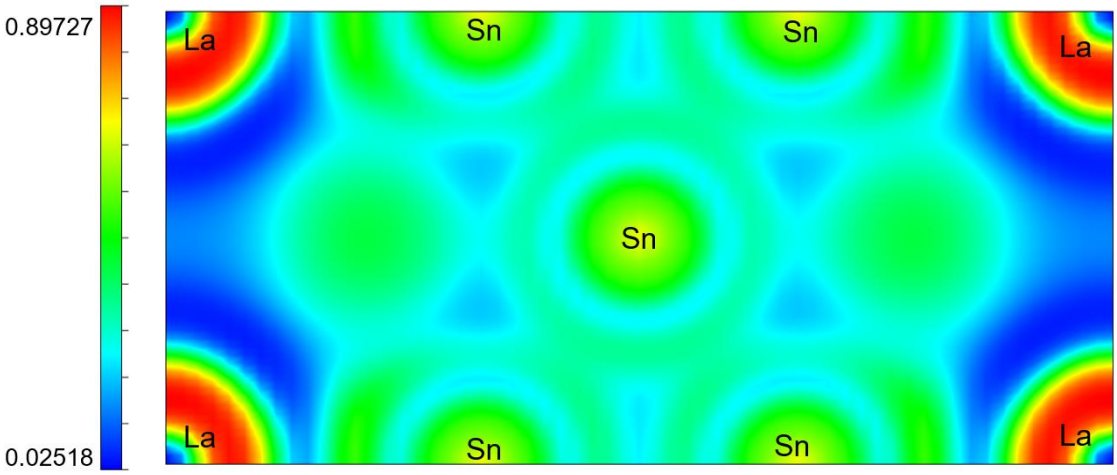

Figure 2 Electron Localization Function map in the (110) plane with labelled atoms constituting the plane and with corresponding scale.

Analysis of the Density of States, see **Figure 3a**, shows a non-zero density of states at the Fermi level (set to 0 eV), as a clear characteristic of a metallic material. The Fermi level passes through a shallow local minimum in the DOS graph. This minimum indicates a relative stabilization of the electronic structure and suggests that the material is electronically relatively stable. This electronic structure is consistent with the metallic nature inherent to intermetallic $LaNi_5$ compounds and supports the delocalized metallic bonding within the $LaSn_5$ structure observed in the ELFCAR analysis. Further, the band structure along high-symmetry paths, see **Figure 3b**, is a further evidence of the metallic nature. It clearly demonstrates that the valence and conduction bands overlap and multiple electronic bands cross the Fermi level (set to 0 eV).

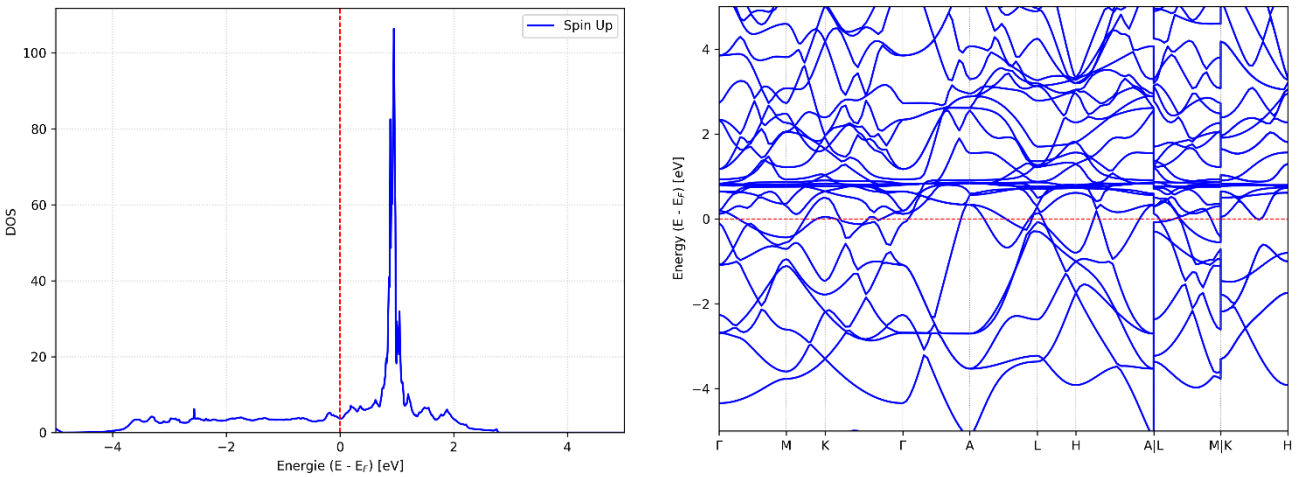

Figure 3 Total Density of States (DOS) (a) and electronic band structure (b), where E_F is set to 0 eV.

Our final step was examining the mechanical stability and elastic properties of the studied phases of $LaSn_5$. We have determined a full tensor of their elastic constants [14]. We present the computed elastic constants (in GPa) as 6×6 matric:

66.73	42.79	28.99	-0.31	0.14	-0.21
42.79	67.25	28.31	-0.05	-0.39	-0.14
28.99	28.31	77.47	0.04	0.08	-0.25
-0.31	-0.05	0.04	-1.03	0.08	0.33
0.14	-0.39	0.08	0.08	-0.94	-0.09
-0.21	-0.14	-0.25	0.33	-0.09	12.06

The initial DFT calculation of the elastic constants indicated that the $LaSn_5$ structure does not strictly meet Born stability criteria because C44 and C55 are smaller than 0. This suggests the compound is likely unstable. To enable further calculation of derived moduli [15], that is impossible with negative eigenvalues of the matrix, the two negative constants were manually set to 1 GPa. Based on the adjusted elastic tensor, the material shows extremely high mechanical anisotropy across all modules (**Table 1**).

Table 1 Derived elastic moduli and anisotropy factors using manually adjusted elastic tensor

	Young's modulus (GPa)		**Linear compressibility (TPa^{-1})**		**Shear modulus (GPa)**		**Poisson's ratio**	
	E_{min}	E_{max}	β_{min}	β_{max}	G_{min}	G_{max}	ν_{min}	ν_{max}
Value	3.4276	62.502	6.2782	8.6262	0.90576	20.061	-0.0040736	0.97167
Anisotropy	18.23		1.374		22.15		∞	

The 3D graph of Young's modulus (**Figure 4**) illustrates the highest rigidity along the *Z* axis and the lowest in the basal plane which causes an extreme anisotropy.

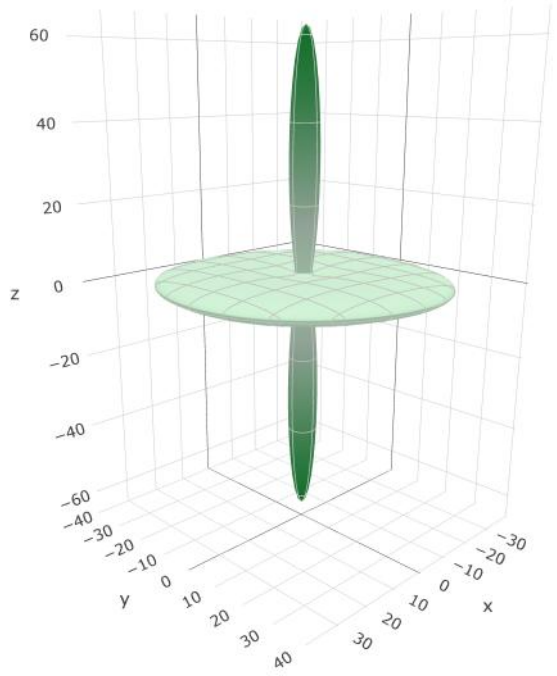

Figure 4 3D graph of Young's modulus of $LaSn_5$ in GPa. The visualization was done by the ELATE [15].

4. CONCLUSION

In this study, we employed Density Functional Theory (DFT) to investigate the structural, mechanical, and electronic properties of the hypothetical intermetallic compound $LaSn_5$, derived from the $LaNi_5$ prototype. This study provided the total energy of formation of $LaSn_5$ (-0.107 eV/atom) which is the essential thermodynamic quantity for CALPHAD modelling of the La-Ni-Sn system. Structurally, the complete substitution of Ni by Sn resulted in a massive volume expansion compared to the reference $LaNi_5$ while preserving the initial hexagonal structure. The $LaSn_5$ structure does not fully satisfy the mechanical stability criteria, indicating that it is metastable. Based on derived moduli, the material exhibits extremely high mechanical anisotropy across all elastic modules. The electronic structure confirms a strong metallic character as evidenced by the multiple bands crossing the Fermi level (E_F) and a non-zero density of states at E_F. However, the Fermi level passes through a shallow local minimum (a pseudo-gap) in the DOS graph. This DOS minimum suggests an electronic stabilization mechanism within the $LaSn_5$ structure, consistent with its thermodynamic stability.

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